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# GEOCHEMICAL CONCENTRATION UNDER SALINE CONDITIONS

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## Abstract

Chemical data are presented for the major and some of the minor elements in salt lakes in two areas of NW. Victoria—Linga and Tyrrell. Whereas evaporation of marine waters concentrates both sodium and magnesium, this latter is depleted in inland basins. This is due to incorporation of magnesium into clay mineral lattices. The mechanism of loss commences with biological reduction of gypsum to give calcium hydroxide. This precipitates magnesium hydroxide which absorbs silica to give poorly crystalline sepiolite. The origin of the high salt content of the lakes is oceanic, with a secondary concentration process by ion-filtration through clay membranes.

## Introduction

In various part of the world, and especially in the interior of continents, there occur large bodies of water of a highly saline nature. These saline lakes are of much wider occurrence than is generally appreciated. In NW. Victoria, because of the low rainfall, flat topography, distance from the coast and ephemeral nature of the drainage pattern, conditions are propitious for large-scale development of saline basins. Two areas have been investigated, the L. Tyrrell system and the Linga lakes system—their localities are shown in Fig. 1. Samples were collected in early September 1963. In open lakes sampling was carried out about 100 ft from shore and at a depth of 1 ft below the surface.

Chemical determinations were carried out on the filtered solutions as soon as practicable. The methods used were as follows:

> Sodium and potassium by flame photometry (Vogel 1961); calcium and magnesium by titrimetry with E.D.T.A. (Welcher 1958); strontium by atomic absorption (David 1962, Willis 1963); chloride, bromide, carbonate, and boron by various titrimetric procedures (Wilson & Wilson 1962); sulphate by turbidimetry using $BaCl_2$ (Vogel 1961); silicon by colorimetry (Mullin & Riley 1955). Analyses were always at least duplicated.

## Results

Chemical data given in Table 1 are expressed as parts per million. High concentrations are reduced by various powers of ten where indicated. In order that comparison may be made between samples, they have been reduced to a common basis by re-calculation of the three main cations, sodium, calcium, magnesium to proportions of 100%, and these have been plotted on a ternary diagram (Fig. 2). Various ratios between the chemical constituents have been calculated and they shed considerable light on the origin and evolutionary sequence of the waters. The cation and anion equivalents are in reasonable balance considering the high salinities.

## Discussion

The proportions of sodium, calcium, and magnesium in the waters have been plotted in Fig. 2 and show that some samples are considerably enriched in sodium

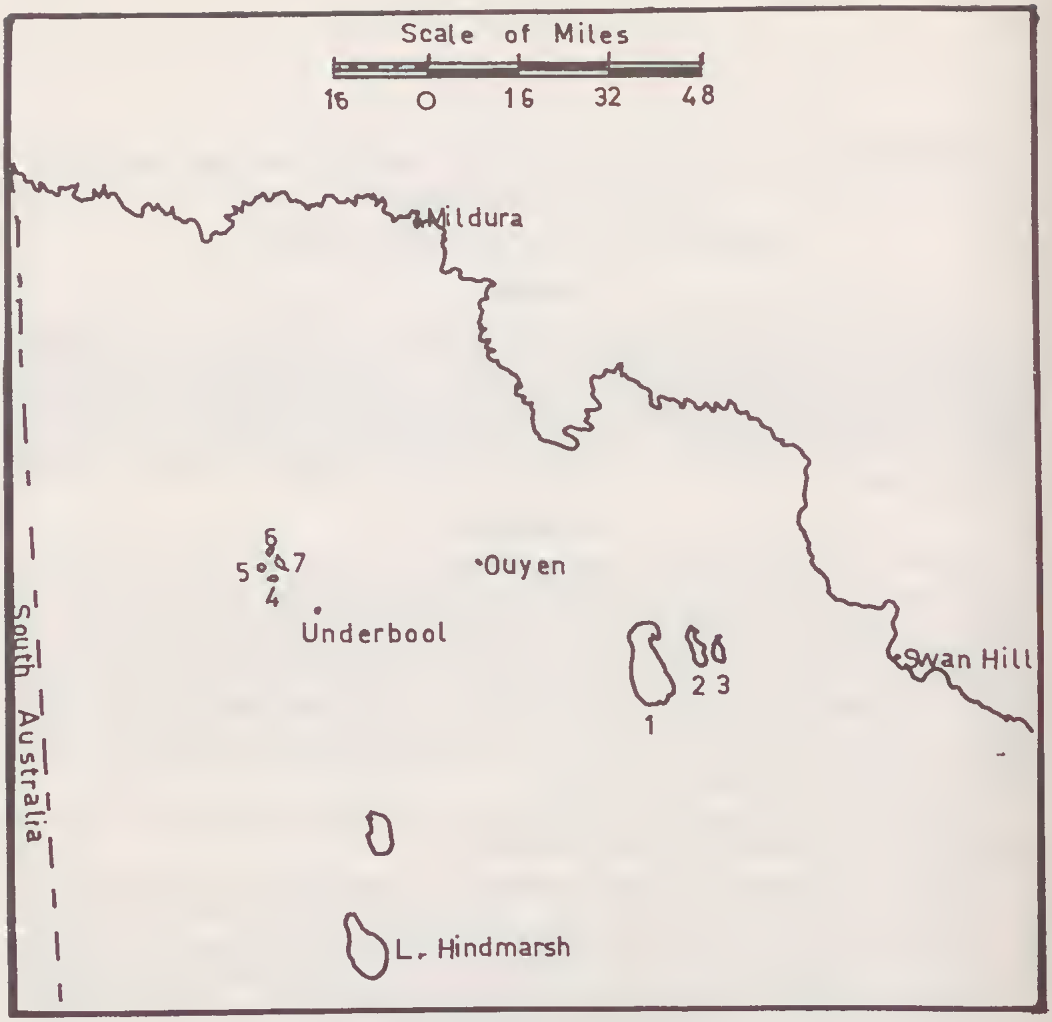

Fig. 1—Locality of samples.
Tyrrell group: 1, 2, 3—Lakes Tyrrell, Wahpool, Timboram.
Linga group: 4, 5, 6, 7—Lakes Nanya, Crosby, Sailor, Crescent.

relative to calcium and magnesium. It has not been possible to include total salinity on the diagram, but generally the higher the salinity, the closer the composition lies to the sodium end of the figure. This trend has been observed with other lake systems, but it has not been possible to plot all of the data because of the overlap on the diagram. Evaporation of oceanic waters has also been plotted on this diagram for three areas—Boccana de Virrila in Peru (Morris & Dickey 1957); Karaboghaz (Clarke 1916); Mediterranean bitterns (Stewart 1963). The concentration trend for these oceanic brines differs from that in a continental setting. Magnesium and sodium are both concentrated.

The loss of calcium relative to sodium and magnesium in inland basins is readily explained. Gypsum is actively being precipitated both as large twinned crystals,

TABLE 1

*Analyses of saline waters of NW. Victoria*

| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Na\cdot10^{-2}$ | 348 | 312 | 940 | 700 | 1140 | 402 | 225 | 360 | 186 | 800 | 870 | 944 | 972 | 1020 | 1054 | 1070 | 105 |
| $K\cdot10^{-1}$ | 26 | 27 | 35 | 29 | 76 | 21 | 28 | 40 | 24 | 36 | 35 | 38 | 39 | 36 | 31 | 35 | 38 |
| $Mg\cdot10^{-1}$ | 344 | 297 | 304 | 243 | 731 | 261 | 228 | 424 | 169 | 163 | 208 | 225 | 291 | 295 | 169 | 169 | 135 |
| Ca | 786 | 694 | 1007 | 806 | 436 | 1100 | 1448 | 1350 | 1233 | 983 | 787 | 787 | 638 | 624 | 871 | 871 | 400 |
| Sr | 9·9 | 9·5 | 3·2 | 3·5 | 3·1 | 9·7 | 12·1 | 11·9 | 11·6 | 9·5 | 6·9 | 6·7 | 6·1 | 6·1 | 1·3 | 1·2 | 8 |
| $Cl\cdot10^{-2}$ | 595 | 532 | 1535 | 1125 | 1842 | 629 | 401 | 636 | 327 | 1274 | 1345 | 1469 | 1541 | 1586 | 1652 | 1703 | 190 |
| Br | 185 | 167 | 152 | 130 | 313 | 82 | 117 | 159 | 96 | 96 | 108 | 118 | 133 | 131 | 97 | 100 | 65 |
| $CO_3$ | 22 | 11 | 36 | 26 | 71 | 92 | 48 | 121 | 88 | 62 | 55 | 61 | 85 | 74 | 48 | 35 | 145 |
| $SO_4\cdot10^{-1}$ | 244 | 203 | 260 | 200 | 804 | 288 | 180 | 256 | 152 | 214 | 411 | 460 | 446 | 480 | 166 | 180 | 266 |
| Si | 7·8 | 3·7 | 0·5 | 0·8 | 0·4 | 1 | 0·8 | 5·5 | 1·1 | 5·6 | 0·5 | 0·6 | 1·3 | 0·9 | 0·2 | 0·2 | 3 |
| B | 8·3 | 5·1 | 0·9 | 0·5 | 2·4 | 2·9 | 5·7 | 0·9 | 6·6 | 3·5 | 1·2 | 0·5 | 3·5 | 3·0 | 1·4 | 1·9 | 4·6 |
| pH | 4·0 | 4·4 | 6·8 | 6·9 | 7·1 | 7·6 | 7·2 | 7·0 | 8·5 | 7·2 | 7·2 | 7·2 | 6·8 | 7·1 | 6·7 | 7·0 |  |
| Na/K | 134 | 116 | 269 | 241 | 150 | 191 | 80 | 88 | 78 | 222 | 248 | 248 | 249 | 283 | 340 | 306 | 28 |
| Ca/Sr | 79 | 73 | 315 | 230 | 141 | 113 | 120 | 113 | 106 | 103 | 114 | 117 | 105 | 102 | 670 | 723 | 50 |
| Cl/Na | 1·7 | 1·7 | 1·6 | 1·6 | 1·6 | 1·6 | 1·8 | 1·8 | 1·8 | 1·6 | 1·5 | 1·6 | 1·6 | 1·6 | 1·6 | 1·6 | 1·8 |
| $Cl/SO_4$ | 24 | 26 | 59 | 57 | 23 | 22 | 22 | 25 | 22 | 60 | 33 | 32 | 35 | 33 | 100 | 95 | 7·1 |
| Cl/Br | 322 | 319 | 1010 | 866 | 588 | 767 | 342 | 400 | 341 | 1328 | 1245 | 1245 | 1159 | 1210 | 1704 | 1703 | 292 |
| $\frac{Na\cdot10^2}{Na+Mg+Ca}$ | 89·2 | 89·5 | 95·9 | 95·6 | 93·6 | 91·5 | 85·8 | 86·3 | 86·4 | 96·8 | 96·8 | 96·9 | 96·5 | 96·6 | 97·6 | 97·6 | 85·7 |
| $\frac{Mg\cdot10^2}{Na+Mg+Ca}$ | 8·8 | 8·5 | 3·1 | 3·3 | 6·0 | 6·0 | 8·7 | 10·4 | 7·9 | 2·0 | 2·3 | 2·3 | 2·9 | 2·8 | 1·6 | 1·6 | 11·0 |
| $\frac{Ca\cdot10^2}{Na+Mg+Ca}$ | 2·0 | 2·0 | 1·0 | 1·1 | 0·4 | 2·5 | 5·5 | 3·3 | 5·7 | 1·2 | 0·9 | 0·8 | 0·6 | 0·6 | 0·8 | 0·8 | 3·3 |

The values in the table are all expressed as parts per million for the analytical data, and are reduced by various powers of ten where indicated. Localities are as follows: 1—Springs in the bed of Tyrrell Ck close to the Sea Lake—Chinkapook road. 2—Lagoon one mile N. of No. 1 and in the Tyrrell Ck deltaic area. 3—L. Tyrrell close to the salt works at the SW. end of L. Tyrrell. 4—Surface water in ponds on the flats adjacent to No. 3. 5—Extreme N. end of L. Tyrrell, water level circa one inch over extensive mud flats. 6—N. end of L. Wahpool. 7—S. end of L. Timboram. 8—N. end of L. Timboram. 9—Transient pool, dry in summer, near Tyrrell Downs. 10—L. Nanya, Linga Lakes, near Ouyen. 11—L. Crosby, S. end, Linga lakes. 12—L. Crosby, central region, Linga lakes. 13—L. Crescent, mid-point on S. side, Linga lakes. 14—L. Crescent, N. end, Linga lakes. 15—L. Sailor, Linga lakes (sampled in morning). 16—L. Sailor, as for 15 (afternoon sample). 17—Ocean—values taken from Goldberg (1963).

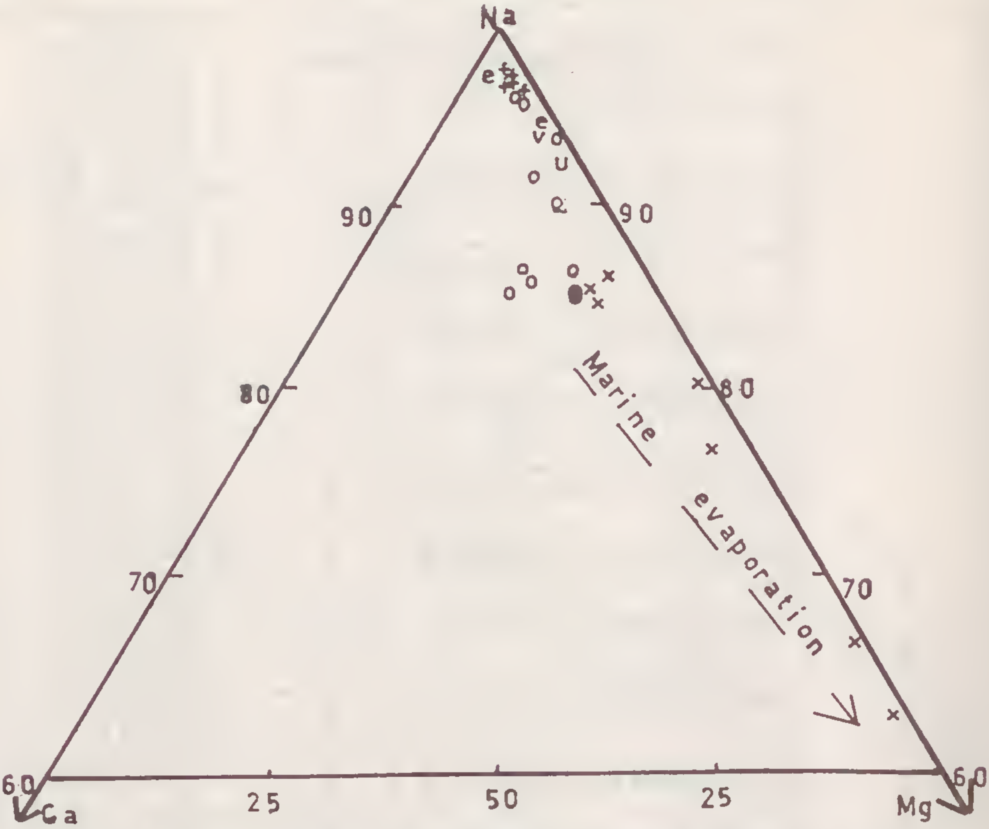

FIG. 2—Portion of the ternary diagram sodium, calcium, magnesium. Compositions of various waters have been plotted as described in the text. Overlap of various points has not been shown in full.

0—Lake Tyrrell group; + Linga lakes group; ●—ocean water; X—concentration of marine waters by evaporation (Boccana de Virilla, Karaboghaz, Mediterranean bitterns, Morris & Dickey (1957), Clarke (1916)); e—Lake Eyre (Bonython 1956); U—Lake Urmi, Persia; V—Lake near Shiraz, Persia (Clarke 1916).

(On evaporation under marine conditions compositions move to the lower right corner as shown. Under terrestrial conditions the compositional move is upwards.)

showing numerous solution and re-growth phenomena, and as fine-grained particles. The large crystals occur in bands and indicate previous strand lines which sometimes may be traced for long distances. They owe their development to variation in solubility, for the edge waters can reach high temperatures during sunny periods. Although, according to the literature, anhydrite should precipitate at high salinity (Posnjak 1940, Stewart 1963), no traces have been found. While this may be because of rapid conversion to gypsum as noted by Zen (1965), the explanation is probably much simpler. It is a common practice in the salt industry to reduce the solubility of gypsum by addition of a small amount (0·5%) of sodium sulphate (Madgin & Swales 1956). In all the uncontaminated waters examined there is excess of sulphate over calcium.

The depletion of magnesium is much more difficult to explain, for in the chemical system investigated magnesium salts are all very soluble. The simple explanation would be to assume concentration to the point where halite is precipitated, the magnesium-rich solutions lost by subterranean flow, then subsequent re-solution of halite. While this might be used to explain, at least partially, the Linga lakes, it may not be applied to the Tyrrell group. During crystallization of halite from water of oceanic composition, bromine is concentrated in the mother liquor. Subsequent solution of the halite gives a liquid of very high Cl/Br ratio (Stewart 1963). The Cl/Br ratios (Table 1) of the Tyrrell waters are too low to apply this explanation of loss by seepage. Numerous workers have explained the loss of magnesium (and perhaps calcium) in natural waters by ion-exchange processes (Hudson & Taliaferro 1925, De Sitter 1947, Degens 1965). This process is not applicable in the waters under discussion for the high sodium content should reverse the process, and any hydrogen exchange would cause low pH. Furthermore, recent work (Hanshaw 1964) indicates that compacted clays have preference for monovalent over divalent ions. A process which could explain the observed facts involves incorporation of magnesium into the lattice of clay minerals and would operate as follows. The presence and high activity of sulphate-reducing bacteria under anaerobic conditions is well known. Baas-Becking & Kaplan (1956) have given evidence of formation of sulphur from gypsum in L. Eyre, and Emery & Rittenberg (1952) have explained sulphate loss in recent sediments as arising from the same cause. All workers agree in classing the process as an important one, and that pH will rise due to $Ca(OH)_2$ formation (Degens 1965). While most authors then assume that the $Ca(OH)_2$ formed will precipitate almost immediately as $CaCO_3$ this is not necessarily true. A process of considerable technological importance to man is the extraction of magnesium from sea water by addition of $Ca(OH)_2$ to give the very insoluble $Mg(OH)_2$, the solubility of which is several orders of magnitude less than that of $CaCO_3$, especially in the presence of $CO_2$. This process must also operate in saline environments, but after precipitation of $Mg(OH)_2$ the $CaCO_3$ might then precipitate, although gypsum seems the more likely possibility. The process is one which would take place in the lacustrine muds. Harder (1965) has shown that freshly precipitated magnesium hydroxide is a very efficient scavenger of silica polymorphs. Quite apart from quartz derived from fluviatile and aeolian transport, silica will be added to the basins from other sources, e.g. opaline silica (Baker 1960). In reducing environments rich in organic matter silica becomes extremely soluble (Emery & Rittenberg 1952). The waters themselves would contain silica largely as the monomer because of pH and low concentration (Iler 1955). The precipitated magnesium hydroxide will scavenge any silica from solution to give an incipient clay mineral.

There are numerous pieces of evidence which substantiate the removal of magnesium by the method outlined. Silicon is comparatively high in the inflowing waters and pH is low (Table 1, No. 1); both alter rapidly. Other workers have recorded the occurrence of magnesium-rich clays from saline environments. Thus, Quaide (1958) recorded chlorite and suspected that it was the stable component; Boynthon (1956) recorded palygorskite at L. Eyre; the present writer has identified poorly crystalline sepiolite in the lacustrine muds of these basins. The type of clay identified and presumably formed by the process outlined above has strongly absorbent properties with respect to organic molecules. The organic products derived from planktonic organisms, e.g. carotenoids and the oily globules surrounding these pigments, would be absorbed (Hodge et al. 1956, Cane 1962). Later diagnetic changes, even pH variation, could release such organic material and under suitable conditions hydrocarbons might arise. Such thoughts are merely speculative, but certainly in accord with modern thought (Buneev 1944, Emery & Rittenberg 1952, Degens 1965). The point of importance in the present discussion is that the black evil-smelling muds of salt lakes are high in organic material, portion of which is of an oily nature. There seems no valid reason, therefore, why hydrocarbon deposits should not arise under highly saline conditions as well as in the usually accepted marine environment.

The geochemistry of the other elements follows normal courses. Potassium is lost relative to sodium as salinity increases due to absorption on clay particles. The Na/K ratios of Table 1 illustrate this point. Behaviour of strontium is complicated by gypsum precipitation. The Ca/Sr ratios rise when gypsum precipitation is active due to occlusion of strontium in the crystals. The rise in $Cl/SO_4$ ratio demonstrates concentration of chloride relative to sulphate.

The Cl/Br ratios are highly diagnostic in indicating the presence or absence of halite deposits in the underlying rocks through which water percolates into the lakes. The Tyrrell group ratios are too low to suggest such deposits, with the exception of No. 5 where halite had been precipitating prior to the time of sample collection. No. 3 & 4 are from an area close to the salt works and illustrate quite clearly by their high ratios, the re-solution of halite and its contaminating effect. The high value for No. 6 is puzzling; it may be due to back wash from soluble salts in the surrounding soils, but the real reason is not known. The Linga group (No. 10-16, Table 1) present a totally different picture. In every sample the high Cl/Br ratio indicates re-solution of salts; in some instances (No. 15 & 16) the lake beds themselves are halite. Despite this, the ratio Cl/Br is not sufficiently high to derive all of the bromide by re-solution of halite. Salts equivalent to the kieserite-carnallite zone would be required to give a Cl/Br ratio of circa 2000 (Kuhn 1955) and the cations of such salts are of insufficient concentration in the waters. Re-solution of halite would give values for Cl/Br which would be even higher. The Cl/Na ratios do not vary greatly, demonstrating that, while both are concentrated, neither undergoes any relative enrichment. They are fairly close to the ratio for oceanic water.

The behaviour of carbonate is a direct reflection of carbon dioxide content, and hence of biological, especially photosynthetic, activity. In Table 1, No. 15 & 16 were taken from the same position. The higher content of carbonate (No. 15) represents material sampled in the early morning; the lower content (No. 16) was sampled in the late afternoon.

The estimation of silicon was carried out by the molybdenum blue method (Mullin & Riley 1955). Because of the low content, all of the silicon estimated would have been present as silica monomer (Iler 1955). Silicon is lost as salinity rises. The Tyrrell group is instructive in showing the high content in the spring waters (Table 1, No. 1) and this rapidly drops as salinity increases. Boron behaves in a similar fashion and is presumably absorbed on to the clay lattice. It has been claimed (Keith & Degens 1959, Potter et al. 1963) that sediments in a marine environment have a higher boron content than terrestrial material. It should be noted that sediments developed under the saline basin conditions described, might also possibly be classed as marine if this method alone was used to characterize strata.

## Origin

The source of the high salinities observed in these waters is probably eventually oceanic, because of various chemical similarities. Direct concentration of oceanic water, either surface or trapped pore water, resulting from the Tertiary marine transgression, does not seem possible because of the time lapse and the limited nature of the lakes. Deposition of salts blown from the arid interior is also rejected, not only because of internal evidence such as Cl/Br ratios, but also physical evidence of lack of aeolian transport in other localities, e.g. Fournier D'Albe (1955) in Baluchistan, and Bonython (1956) in L. Eyre.

Concentration from rain water, which normally contains small quantities of oceanic salts, is known as the 'cyclic salt hypothesis'. This has many adherents in Australia and elsewhere (Anderson 1941, 1945; Collins & Williams 1933; Hutton & Leslie 1958; Jack 1921; Jackson 1965; Loewengart 1962; Riffenberg 1926).

In rain, calcium increases relative to other cations with distance from the sea. This has been explained as resulting from small particles of calcium sulphate which are whirled aloft and not carried down by rain-out to such an extent as the more soluble constituents. These latter are deliquescent, form droplets, and so are lost closer to the coast (Ericksson 1952, 1959; Gorham 1958; Junge 1954; Squires 1956; Sugawara et al. 1949; Twomey 1955).

Woodcock et al. (1953) observed that bursting bubbles in the sea were very efficient removers of the surface oily layer resulting from planktonic organisms. This organic material should be highly concentrated in spray and because it possesses cation-exchange properties, it has been suggested as an explanation of differential sodium to chlorine enrichment in rain-water (Ericksson 1959). Since divalent ions absorb more strongly than monovalent, calcium should concentrate with the organic material. The present writer would suggest that such organo-calcic complexes should be hydrophobic, dry rapidly, and thus remain as aerosols. They would, in the interior of arid continents, be lost by fall-out as well as occasional rain-out. Much of the fine loess-like gypsum of the Australian interior (kopi) may have arisen by this mechanism and not by precipitation from a lucustrine or estuarine environment. The grain-size of the fine-grained kopi is not inconsistent with the type of material obtained technologically by spray-drying.

To explain the saline basins being discussed in this paper, as representing residual liquor due to evaporation of rain water 'in situ', does not seem to be satisfactory to the author. There are many areas in the region where the waters never beome more than slightly brackish, and these should also show high salinities, especially as they may often evaporate compltely. The problem is one which presents certain similarities to underground waters. With these latter it is current theory that salinity rise is due to differential ion filtration through negativly-charged clay membranes (Russell 1933, De Sitter 1947, Bredehoeft et al. 1963). In the geological section drawn by Johns & Lawrence (1964) a thick band of clay is shown as overlying sand, carbonaceous clay, and some lignite. This would be an ideal membrane under the above scheme of concentration. Fracturing of the membrane would give access to the saline waters concentrated beneath. In the Tyrrell region there is some evidence for buried ridges and valleys and saline springs are largely responsible for the lake waters (Hills 1939). Although the eventual source of the salts is oceanic, it is more than likely that differential dialysis is also an important process in the concentration process.

In conclusion, it is pertinent to note that different clays might well be expected to behave in varying fashions in their ion-membrane dialysis properties. Different rocks, or their weathered counterparts, might be expected, therefore, to concentrate salts in different fashions. The statement of Plinius thus takes on a new and more vivid meaning. 'Tales sunt aquae, qualis terra per quum fluunt' (Waters take their nature from the rocks through which they flow).

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